SAMPLE PREPARATION FOR, AND CURRENT STATUS OF, THE ARGONNE PREMIUM COAL SAMPLE PROGRAM*

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ABSTRACT

The Argonne Premium Coal Sample Program includes eight coals (Upper Freeport, Wyodak-Anderson, Illinois #6, Pittsburgh, Pocahontas #3, Utah Blind Canyon, Lewiston-Stockton and Beulah-Zap seams) chosen to provide a range of chemical composition, including sulfur content, maceral content and geographic distribution. One of the purposes is to provide a set of pristine samples for comparison and correlation. They have been collected in ton-sized batches and processed to provide a minimal exposure to oxygen, thoroughly mixed, and packaged in borosilicate glass ampoules containing either 5 grams of -100 mesh or 10 grams of -20 mesh material. This material has been analyzed by a number of laboratories, including a round robin with Commercial Testing and Engineering Co. Further data are being added to an analytical data base as they become available. Over 190 shipments have been made to over 110 different users. Research is currently being carried out in almost every area of coal science with these samples.

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INTRODUCTION

Goals:

The Premium Coal Sample Program was initiated at the Argonne National Laboratory about five years ago to provide the basic coal research community with a small number of carefully selected, collected, processed packaged and analyzed samples. The techniques of mixing, sealing and storage are intended to provide a large number of uniform samples that will be stable over a long time, and will permit reproducible experiments to be carried out at different times and laboratories.

Selection of Samples:

The coals included in the program were selected to give a range of composition in terms of the carbon, sulfur, hydrogen and oxygen contents. A cluster analysis involving data from over 200 channel samples in the existing Pennsylvania State University database was used to provide eight ranges of composition, from which the chemical composition characteristics of the eight samples were chosen. In addition they were selected to give a range of rank, geographical distribution, and maceral content.

In the order collected, these eight coals are:

#	Seam	Origin	Rank
1	Upper Freeport	PA	MVB
2	Wyodak-Anderson	WY	SUB
3	Illinois #6	IL	HVB
4	Pittsburgh	PA	HVB
5	Pocahontas #3	VA	LVB
6	Utah Blind Canyon	UT	HVB
7	Lewiston-Stockton	WV	HVB
8	Beulah-Zap	ND	LIG

The abbreviations are: LIG = lignite, SUB = subbituminous, HVB = high volatile bituminous, MVB = medium volatile bituminous, LVB = low volatile bituminous.

Collection:

Details of the procedures for collection have been given in earlier reports (1-8). In brief, the samples from underground mines were collected from freshly exposed blocks of coal, the thickness of the seam. Typical samples were about 1 1/2 tons. For thick underground seams (#3,4,5,6,7), the 55 gallon stainless steel drums were taken to the seam face, and representative samples were placed directly into the drums. For the thinner seam (#1) the sample was taken to the surface in double plastic bags. Surface mine samples (#2 and 8) were obtained from core samples.

Processing and Packaging:

At the surface the drums were purged with enough argon to reduce the oxygen content to 100 ppm, and quickly transported in a temperature-controlled semi-trailer to Argonne National Laboratory (ANL) for processing. AT ANL, the drums were weighed, placed into airlocks, purged, the contents were crushed, pulverized to -20 mesh, thoroughly mixed, and the contents were packaged. Half the batch was reground to -100 mesh, and then packaged. Packaging included placing about 80% of the coal in carboys of borosilicate glass for long term storage. The balance went into amber borosilicate glass ampoules of 10 grams of -20 mesh or 5 grams of -100 mesh material. The oxygen content of the packaging facility was maintained below 100 ppm at all times, and was typically about 30 ppm.

CURRENT STATUS

Inventory - Long Term Supply:

The ampoules and carboys are kept in a dark air-conditioned storage room. About 10,000 of the 5 gram ampoules and 5,000 of the 10 gram ampoules were made for each sample. Initially about 120,000 samples were placed in storage with about 550 of the 5 gallon carboys. As shipments deplete the inventory, then carboys can be placed in the packaging facility and additional ampoules filled and sealed to replenish the inventory. The current demand is such that the supply of ampoules should not need replenishing for another 6 years. The Illinois #6 sample is the most frequently requested.

Homogeneity:

Samples were taken during the processing to be irradiated and counted for homogeneity analysis. The results indicate that the samples were well mixed. Additional samples have been sent to a number of laboratories for analysis. Commercial Testing and Engineering Company performed a round robin analysis for the proximate analysis, and also carried out a number of ultimate, ash and other analyses as well.

Stability:

Stability analyses are carried out in two ways. The ampoules are routinely sent to the Analytical Chemistry Laboratory at ANL for gas analyses. The gas inside of the ampoules is analyzed for oxygen, hydrogen, nitrogen, carbon dioxide, methane, and other hydrocarbon gases. The results have indicated that no oxygen is entering the ampoules and the interior gas has a generally stable composition, with some tendency to liberate methane and carbon dioxide. The other stability study involves the gieseler plasticity analysis for the bituminous samples. These samples are sent at half year intervals for continued monitoring.

Analyses:

Other laboratories are encouraged to make the results of their analytical efforts known to the author so that they may be incorporated into a compendium of results for the benefit of all of the sample users. Table 1 gives a listing of the results for the analyses done by CT&E. The modified Parr formula used for the Dry mineral matter free content calculations was:

Mineral matter(dry) = 1.13 Ash + 0.47 Pyritic S(dry) + 0.50 Cl (dry)

Other Studies:

This unique set of samples can advantageously be used to carry out a number of studies in a "round-robin" type of effort to help different laboratories compare their results, and develop an understanding of the differences in the coal samples. A study of the NMR characteristics of the samples is being planned, with the results to be shared near the end of 1989.

Shipments:

The acceptance and popularity of the samples may be gauged by the number of shipments, re-ordering and scope of work done with them. At the time of the writing, over 190 shipments had been made. These included over 110 different laboratories and investigators. Several of these have requested four different batches of samples. The shipments have gone approximately about 2/3 to academic institutions, and the rest about evenly divided between industrial and governmentally supported laboratories. About 5% of the shipments have gone to countries other than the U. S. A. The number of ampoules shipped has exceeded 6,000.

USGS Circulars - Geology and Geography:

In addition, the United States Geological Survey, which supervised the collection of the samples, is preparing a series of USGS Circulars, which will summarize the geological and geographical information of general interest about these samples. These may be obtained directly from the USGS.

Newsletter:

A newsletter has been initiated to provide current information of value to all recipients of the samples. The quarterly publication gave the contents of this symposium, and announced the development of a bibliography of references to the use of the Argonne Premium Coal Samples. All recipients of samples are asked to provide references to reports, journal articles and other public information so that this information may be shared with other investigators.

Types of Research Work:

The types of research being done with the samples are about as diverse as the research being done on coal. The symposia that follows will give a representative sample, but certainly does not include all of the work that is being done. The major fields include: structural studies, determination of the functional groups qualitatively and quantitatively in the coal, coalification, pyrolysis, liquefaction and gasification, sulfur removal, new methods of analysis and others.

Symposia:

This symposium is the second in a series devoted to research done with the Argonne Premium Coal Samples. The first, held in New Orleans in September, 1987 had 23 papers on a variety of topics. The organization this year is based on the subject matter of the individual papers. The range of work is such that a number of papers are finding their way into symposia on topics of special interest such as coal liquefaction, and this trend will probably continue.

Future Activities:

The APCSP will continue to provide samples and information about these samples to the users. It is planned to provide a data handbook to give in one document the most frequently requested information. This will include the results of the analytical work that is reported to the author, and special studies which have been arranged to provide for a reasonably complete set of information.

Further, individual studies may be initiated to respond to certain findings of potential interest to the user community. The observation of increased concentrations of methane and carbon dioxide in some of the ampoules led to speculation that anaerobic bacteria may be present with the samples. An effort is underway

to culture bacteria from samples of coal from each of the batches. The results of this effort will be described at a future meeting.

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Table 1. As-received and maf values Calculated from Dry Data from CT&E

Coal	UF	WY	IL	PITT	POC	UT	WV	ND
AR H2O	1.13	28.09	7.97	1.65	0.65	4.63	2.42	32.24
AR Ash	13.03	6.31	14.25	9.10	4.74	4.49	19.36	6.59
AR VM	27.14	32.17	36.86	37.20	18.48	43.72	29.44	30.45
AR S	2.29	0.45	4.45	2.15	0.66	0.59	0.69	0.54
AR Btu	13315	8426	10999	13404	14926	13280	11524	7454
Dry Ash	13.18	8.77	15.48	9.25	4.77	4.71	19.84	9.72
Dry VM	27.45	44.73	40.05	37.82	18.60	45.84	30.17	44.94
Dry S	2.32	0.63	4.83	2.19	0.66	0.62	0.71	0.80
Dry Btu	13467	11717	11951	13629	15024	13925	11810	11001
Dry C	74.23	68.43	65.65	75.50	86.71	76.89	66.20	65.85
Dry H	4.08	4.88	4.23	4.83	4.23	5.49	4.21	4.36
Dry N	1.35	1.02	1.16	1.49	1.27	1.50	1.25	1.04
Dry Cl	0.00	0.03	0.05	0.11	0.19	0.03	0.10	0.04
Dry F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyritic S	1.77	0.17	2.47	1.32	0.15	0.24	0.16	0.14
Sulfate S	0.00	0.03	0.01	0.01	0.03	0.03	0.03	0.03
Organic S	0.64	0.43	2.01	0.81	0.48	0.35	0.52	0.63
MAF C	85.50	75.01	77.67	83.20	91.05	80.69	82.58	72.94
MAF H	4.70	5.35	5.00	5.32	4.44	5.76	5.25	4.83
MAF N	1.55	1.12	1.37	1.64	1.33	1.57	1.56	1.15
MAF Org S	0.74	0.47	2.38	0.89	0.50	0.37	0.65	0.70
MAF Cl	0.00	0.03	0.06	0.12	0.20	0.03	0.12	0.04
MAF F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAF O	7.51	18.02	13.51	8.83	2.47	11.58	9.83	20.34
MAF Btu	15511	12843	14140	15018	15777	14613	14733	12185

Dmmf values based on modified Parr formulas

Coal	UF	WY	IL	PITT	POC	UT	WV	ND
Dry Ash	13.18	8.77	15.48	9.25	4.77	4.71	19.84	9.72
Dry VM	27.45	44.73	40.05	37.82	18.60	45.84	30.17	44.94
Dry S	2.32	0.63	4.83	2.19	0.66	0.62	0.71	0.80
Dry Btu	13467	11717	11951	13629	15024	13925	11810	11001
MM Parr	15.73	10.00	18.68	11.13	5.56	5.45	22.54	11.07
Dry C	74.23	68.43	65.65	75.50	86.71	76.89	66.20	65.85
Dry H	4.08	4.88	4.23	4.83	4.23	5.49	4.21	4.36
Dry N	1.35	1.02	1.16	1.49	1.27	1.50	1.25	1.04
Dry Cl	0.00	0.03	0.05	0.11	0.19	0.03	0.10	0.04
Dry F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyritic S	1.77	0.17	2.47	1.32	0.15	0.24	0.16	0.14
Sulfate S	0.00	0.03	0.01	0.01	0.03	0.03	0.03	0.03
Organic S	0.64	0.43	2.01	0.81	0.48	0.35	0.52	0.63
Dmmf C	88.08	76.04	80.73	84.95	91.81	81.32	85.47	74.05
Dmmf H	4.84	5.42	5.20	5.43	4.48	5.81	5.44	4.90
Dmmf N	1.60	1.13	1.43	1.68	1.34	1.59	1.61	1.17
Dmmf Org	0.76	0.48	2.47	0.91	0.51	0.37	0.67	0.71
Dmmf Cl	0.00	0.03	0.06	0.12	0.20	0.03	0.13	0.04
Dmmf F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dmmf O	4.72	16.90	10.11	6.90	1.66	10.88	6.68	19.13
Dmmf Btu	15980	13020	14696	15336	15908	14728	15247	12370